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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### A process of Treating Cellulosic Materials

We, DEERING MILLIKEN RESEARCH CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of P.O. Box 1927, Spartanburg, South Carolina, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel process for the rapid wet cross-linking of hydrated cellulosic materials to impart wet configurational memory thereto, more particularly to the strong base catalyzed cross-linking of cellulosic materials with epichlorohydrin.

In British Patent Specification No. 855547 there is disclosed a method of wet cross-linking cellulosic fabrics with epichlorohydrin while the fabric is impregnated with moisture and strong base catalyst. The reaction rate of this method is such that several hours is usually required to obtain complete reaction at room temperature. As would be expected, this reaction time can be reduced by heating the fabric while impregnated with the moisture, strong base and epichlorohydrin. However, because of the volatility of the epichlorohydrin, this method of accelerating the reaction is not practical in a batch-wise process above 60°C. Also, in a batch-wise process, above 90°C. the efficiency of the reaction apparently is reversed and the desired cross-linking reaction does not proceed properly so that much less flat drying properties are imparted to the cellulosic material. Thus, the cross-linking of cellulosic materials with epichlorohydrin has heretofore had to be conducted in a time consuming batch-wise procedure requiring from one-half hour to several hours for completion of the reaction.

It was surprising therefore to find that, when following the process of this invention, the desired cross-linking reaction proceeds efficiently and very rapidly at temperatures substantially above those which result in a poor

reaction under the prior batch-wise procedures.

Another surprising effect observed when following the process of this invention is that the strength loss inherent in cross-linking of cellulosic materials is less for any given degree of flat-dry performance than is obtained when the cross-linking reaction is achieved by applying liquid epichlorohydrin to the cellulosic material in a batch-wise manner.

It is, therefore, an object of this invention to provide a rapid method for cross-linking cellulosic materials with epichlorohydrin while the material is impregnated with moisture and strong base to impart wet resiliency thereto.

Another object is to provide a continuous process for cross-linking cellulosic material, preferably cotton fabric, with epichlorohydrin.

Still another object is to provide a method of reducing the strength loss obtained when cross-linking cellulosic materials with epichlorohydrin to impart wet configuration memory thereto.

According to this invention, a process for the rapid cross-linking of hydrated cellulosic materials with strong base (as herein defined) catalysed epichlorohydrin to impart wet configurational memory thereto comprises contacting the material impregnated with from 0.5% to 130% moisture and from 0.75% to 15% strong base catalyst calculated as NaOH, both calculated on the weight of the dry cellulosic material, with gaseous epichlorohydrin in a closed system while the material is in the selected configuration, and maintaining the material in contact with the gaseous epichlorohydrin in the selected configuration in the closed system for at least 5 seconds until at least 0.75% of strong base catalyst, calculated as NaOH and on the weight of the dry cellulosic material has been consumed.

In the preferred form of this invention, cellulosic material in web form, preferably woven fabric, which is uniformly impregnated with up to 100% moisture and 1—5% strong base catalyst is passed continuously in the

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selected configuration into contact with hot epichlorohydrin vapors until substantially all of the catalyst has been consumed and is then heated to a temperature above the boiling point of epichlorohydrin until substantially all of the epichlorohydrin is removed from the material.

The term "wet configurational memory" as used herein means that the cellulosic material treated according to the present process tends to return, after being distorted or crumpled while in the wet state, to the configuration in which it was in when the cross-linking reaction took place. In the case of yarn, this means that the yarns can be compacted while wet and if they were cross-linked in an uncrumpled state, the yarns will tend to straighten themselves if permitted to do so. Fabrics knitted or woven from such treated yarns will also resist wrinkling while being washed. If the yarn is cross-linked in a crumpled position, the resulting yarn and fabric prepared therefrom will have a bulked effect and will resist being distorted into a smooth configuration. When fabrics are treated in a smooth, wrinkle-free state, the cross-linked fabric will thereafter resist wrinkling in the wet state. These fabrics can therefore be washed and spin-dried in an automatic washer or wrung out by hand and will dry on the line substantially wrinkle-free.

Cellulosic materials which can be cross-linked according to the process of this invention are those which are normally cross-linked to impart wet configurational memory thereto, e.g., natural and regenerated cellulose, and cellulose derivatives having only a portion of the free cellulosic hydroxy groups esterified or etherified so that at least 1.8 free hydroxy groups per anhydroglucose unit remain, e.g., lower-hydrocarbon esters, including the acetate, propionate, butyrate and benzoate and sulfate, phosphate, and aryl and alkyl sulfate esters, and lower-alkyl ethers, including methyl, ethyl, and hydroxyalkyl, including hydroxyethyl, and carboxymethyl and carboxyethyl ethers. The natural cellulosic materials can be in the form of cotton, linen, jute or flax, and the synthetic cellulosic materials can be in the form of filament or staple viscose rayon, both unmodified and modified, e.g., the polynosic rayons. The cellulosic material can also have had a prior textile resin treatment, e.g., with urca-formaldehyde, melamine-formaldehyde, cyclic ethylene urea, dihydroxy cyclic ethylene urea, triazone, or other commonly employed textile resin, so that the material already has substantial dry configurational memory and, to a lesser degree, wet configurational memory.

The novel process is directed primarily and preferably to cellulosic materials in web form, including knitted, non-woven and woven fabrics, but the advantages of this invention can also be achieved by treating the cellulosic fibers, yarns or threads employed to produce

these webs. The preferred cellulosic material is cotton fabric which is preferably woven, e.g., printcloth, broadcloth and sheeting. Although the process will ordinarily be conducted on cellulosic material consisting entirely of cotton or viscose rayon, the process is equally applicable to such yarns and fabrics also containing synthetic filaments or fibres, e.g., the glycol-terephthalate polyester, nylon, and polyacrylic fibres. Preferably the cellulosic material comprises at least 40% or more by weight of the material to be treated and more desirably 60% or more.

The strong base catalysts for the cross-linking reaction are defined as bases having a pH of at least 10 as a 1% by weight aqueous solution and include the alkali-metal hydroxides, e.g., sodium hydroxide and potassium hydroxide, the quaternary ammonium hydroxides, e.g., trimethylphenyl ammonium hydroxide, and alkali-metal salts which, in the presence of moisture, produce a strongly alkaline solution, e.g., the alkali-metal sulfides and alkali-metal silicates. When the salts are employed, they should be employed in amount which will impart an alkalinity to the solution in about the same range as that obtained when an alkali-metal hydroxide is employed. Because the cellulosic material tends to lose strength proportionally to the amount of strong base catalyst present therein during the reaction, the amount of catalyst present initially on the material desirably is less than 10%, calculated stoichiometrically as NaOH and on the weight of the dry fabric, preferably between 1% and 7% and more preferably between 1% and 5%, e.g., between 2.0% and 4%. The optimum amount of catalyst which should be present in the fabric under any given set of conditions will depend in part upon the manner in which the strong base is applied, the total moisture present during the reaction and the total reaction time. For example, if the catalyst is applied as a relatively dilute, e.g., 2-5%, aqueous solution by padding so that the material is completely wetted out, the amount present on the fabric is ideally between 2 and 4%. If the catalyst is applied as a relatively concentrated aqueous solution, e.g., 10-50%, in limited amounts, e.g., by means of a print roll, the amount applied is ideally between from 0.75 to 2.0%. If between 1% and 5% is applied, the reaction can be continued until substantially all of the strong base is consumed.

As stated above, the cross-linking reaction is conducted while the cellulosic material is impregnated, initially at least, with moisture as well as the strong base catalyst. Moisture is most conveniently provided by applying the strong base catalyst to the fabric in the form of an aqueous solution. The amount of moisture present during the reaction, while not critical within a fairly wide range in producing wet configurational memory in the mate-

rial, can affect the amount of dry configurational memory imparted to the cellulosic material. For example, if the total moisture present in the material exceeds 15%, calculated on the dry weight of the material, wet configurational memory is imparted to the material but little if any significant dry configurational memory. On the other hand, when the total moisture content is below 15%, good wet and dry configurational memory can be imparted to the material. The minimum amount of moisture which should be present to ensure adequate cross-linking is very low, i.e., in the range of 0.5—2%, which is considerably lower than the moisture content of cotton at normal atmospheric humidities. The maximum moisture which should be present to ensure adequate cross-linking is 130%, but is preferably below 100%, and most preferably below 85%, calculated on the dry weight of the fabric. If the moisture level of the cellulosic material after being impregnated with strong base catalyst is too high, an intermediate drying step can be introduced to reduce the total moisture level, e.g., to 3—15%. Pre-heating of the material can also be employed to reduce excessive cooling in the reaction chamber and excessive condensation of liquid epichlorohydrin on the fabric.

As stated above, the moisture and strong base can be applied by padding, applicator roll, print roll or spraying, so long as it is uniformly distributed throughout the material in a manner which will avoid undesired distortion of the material, e.g., crinkling and puckering. If the strong base is deliberately applied unevenly, a plisse effect can be produced in fabrics or a wool-like effect with fibers. Ordinarily, it is desired to apply the strong base uniformly to fabric, e.g., by immersing in an excess of an aqueous solution of the selected strong base and squeezing through nip rolls to remove the excess base and moisture, as flat drying properties are imparted to fabric under these conditions.

The selected material is then passed into a closed system for contacting with epichlorohydrin. The term "closed system" means that the system is sealed against extraneous leakage of epichlorohydrin vapors. Obviously, an entrance and exit for the cellulosic material must be provided but leakage of vapors can be avoided by vapor seals. Also, an outlet above the condensation system must also be provided, but significant amounts of epichlorohydrin will not escape if the condensation system is adequate. The cellulosic material should be in the desired configuration while being in contact with the epichlorohydrin and impregnated with the strong base catalyst. Ordinarily, this will mean, e.g., that fabric is passed open width into the chamber and maintained in a smooth, wrinkle-free condition during the reaction period.

A dwell period must be provided for con-

tacting the material with epichlorohydrin vapors for a time sufficient to consume at least 0.75%, calculated as NaOH and on the weight of the dry cellulosic material, of strong base catalyst, e.g., 5 seconds to 10 minutes, preferably 30 to 300 seconds. This can be achieved with a Benteler batcher system or a festoon system, if the material is in web form, or by a series of rolls or aprons if the material is in yarn or untwisted fiber form.

The epichlorohydrin can be contacted with the cellulosic material in vapor form by providing a sump-type arrangement heated, e.g., with steam coils, to maintain a reservoir of liquid epichlorohydrin at its boiling point, and passing the cellulosic material above the surface of the boiling epichlorohydrin. The material should not be passed into contact with the surface of the boiling epichlorohydrin as this adversely affects the process.

The gaseous epichlorohydrin rapidly reacts with the cellulosic material while at the same time consuming the strong base catalyst and removing some or all of the water in the material. Means preferably should be provided to remove this water from the system to prevent a build-up of it therein, e.g., by a condensor system with a trap arrangement whereby the water is separated from the epichlorohydrin as both are condensed. As the epichlorohydrin consumes the strong base catalyst while reacting with the cellulosic material, the reaction is self-terminating if sufficient reaction time is provided. Thus, it is not necessary to avoid contacting the material with an amount of gaseous epichlorohydrin considerably in excess of the theoretical amount required and, in fact, it is desirable to do so. It is preferred that the material be contacted with an amount of gaseous epichlorohydrin at least equivalent in moles to the amount of strong base present on the material, but lesser or greater amounts can be employed, if desired, e.g., from 0.5 to 20%, calculated on the weight of the dry cellulosic material.

When the cross-linking reaction has proceeded to the desired extent or is complete, the cellulosic material will be saturated with impregnated excess epichlorohydrin, particularly if the fabric has not been maintained at a temperature at or above the boiling point of epichlorohydrin. To improve the economics of the process and to avoid handling the material impregnated with epichlorohydrin in the open, it is preferably thereafter heated, e.g., with steam heated dry cans or by radiant means to a temperature above the boiling point of epichlorohydrin. To prevent recondensation of the epichlorohydrin in the material, this heating step is preferably conducted above the condensation height of the epichlorohydrin in the closed chamber, e.g., by maintaining the heating means above the level where the epichlorohydrin vapors are condensed by the cooling system, or conducted in a separate portion of

the closed chamber which is maintained at a temperature above the boiling point of epichlorohydrin.

- 5 The textile material can thereafter be washed in the usual fashion, if desired, to remove any traces of reactants or reaction by-products.

- 10 The following Examples are illustrative of the process of this invention. Percentages are expressed on a weight basis throughout these Examples.

#### EXAMPLE 1

- 15 Bleached and mercerized 3.19 yd./lb. at 40" 136 x 64 cotton broadcloth having filling tensile strength of about 62 lbs. is passed open width continuously into a pad box containing 3.5% aqueous NaOH, then through squeeze rolls to provide an 80% pick-up thereof, and then through vapor seals into a closed chamber. The chamber is equipped near its top with a water cooled condensor having a Starke-Dean trap which returns the condensed epichlorohydrin to the bottom of the chamber and removes water from the system. The bottom of the chamber has steam coils which heat the liquid epichlorohydrin to its boiling point. A float device attached to a source of epichlorohydrin maintains a constant volume of epichlorohydrin in the system. Above the condensation level of the epichlorohydrin are dry cans steam heated to above the boiling point of epichlorohydrin. Below the condensation level of the epichlorohydrin is provided a festoon system for moving the fabric open width and in a wrinkle-free condition. The NaOH impregnated fabric is passed continuously through the festoon system at a speed that provides a 120 second exposure time to the epichlorohydrin vapors. The fabric is then passed over the dry cans so that substantially all of the epichlorohydrin is removed from the fabric, which is then removed from the closed chamber through a vapor seal and into washing tanks. The resulting fabric has a wet crease recovery angle of at least 140°, filling tensile of at least 30 lbs. and will rate at least 4.0 by the standard flat drying test

involving passing a square of the fabric through the spin cycle of an automatic washer containing a standard load to damp dry the fabric and then line drying the fabric and then comparing the degree of wrinkling of the fabric with standard plastic samples under low angle single source lighting conditions.

Any or all of the following variations can be introduced into the above-described system.

1. The concentration of the NaOH can be varied between 0.75% and 15%, e.g., 1%, 2%, 3%, 4% or 5%, based on the dry weight of the fabric, depending on the degree of flat drying desired and the amount of residual strength to be retained.

2. Pick-up of the NaOH solution can be varied between 35% and 100%, e.g., 40%, 50%, 60%, 70%, 90% or 100%.

3. The exposure time can be varied between 30 seconds and 300 seconds with the shorter exposure times preferably being employed in conjunction with higher NaOH concentrations.

4. The heating of the fabric on the dry cans to remove residual epichlorohydrin can be omitted or replaced by radiant heating.

5. KOH can be substituted for the NaOH.

6. In all of the above-described reaction conditions, the dwell time can be adjusted to consume all or any desired portion of the strong base catalyst but in each instance, the minimum dwell time of 30 seconds will result in at least 0.75% of the NaOH being consumed. The amount of catalyst consumed will increase with increasing dwell times and at at the maximum of 300 seconds substantially all the NaOH is consumed.

#### EXAMPLE 2

85 Samples of 180 count percale cotton sheeting containing varying amounts of aqueous sodium hydroxide, obtained by immersing the fabric in a caustic solution of the selected concentration and blotting to a pick-up of 80—100%, are exposed in a closed system to the vapors from boiling epichlorohydrin for various periods of time, washed thoroughly and then tested for wet crease recovery. Results obtained from such experiments are

experiments are shown in Table 1 below.

TABLE I

Sample	NaOH Concentration % based on dry weight of fabric	Exposure Time (Seconds)	Wet Crease Recovery Angle (Filling)
Control			79°
1	1.2%	300	106°
2	2.4%	30	100°
3	do	300	118°
4	12%	30	100°
5	do	120	133°
6	do	300	145°
7	do	30*	118°
8	do	120*	128°
9	15%	30	118°
10	do	300	137°

\* Fabric then heated at 117°C. to drive off all epichlorohydrin condensed on fabric before washing.

In every instance, at least 9.75% of NaOH is consumed.

## EXAMPLE 3

The procedure of Example 2 is followed on 4.00 yd./lb. bleached and mercerized 80 x

80 cotton printcloth. The results of such experiments are shown in Table II below.

TABLE II

Sample	NaOH Concentration	Exposure Time (sec)	Wet Crease Recovery Angle (Filling)	Strip Tensile (Filling) (Lbs.)
Control	2.5%	0	92°	39.5
1	do	60	116°	33.8
2	do	120	144°	23.3
3	10%	60	145°	25.0
4	do	120	156°	22.0
5	15%	30	144°	31.8

## WHAT WE CLAIM IS:

1. A process for the rapid cross-linking of hydrated cellulosic materials with strong base (as herein defined) catalysed epichlorohydrin to impart wet configurational memory thereto which comprises contacting the material impregnated with from 0.5% to 130% moisture and from 0.75% to 15% strong base catalyst calculated as NaOH, both calculated on the weight of the dry cellulosic material, with gaseous epichlorohydrin in a closed system while the material is in the selected configuration, and maintaining the material in contact

with the gaseous epichlorohydrin in the selected configuration in the closed system for at least 5 seconds until at least 0.75% of strong base catalyst, calculated as NaOH and on the weight of the dry cellulosic material, has been consumed.

2. A process according to claim 1, in which the material is continuously passed into the closed system.

3. A process according to claim 1 or claim 2, in which the strong base catalyst is an alkali metal hydroxide.

4. A process according to any of claims

1—3, in which the starting cellulosic material is impregnated with up to 100% moisture and between 1 and 5% strong base.

5 5. A process according to any of the preceding claims, in which the starting cellulosic material is impregnated with up to 15% moisture and between 1 and 5% strong base.

10 6. A process according to any of the preceding claims, in which the cellulosic material contains between 2% and 4% strong base.

7. A process according to any of the preceding claims, in which the cellulosic material is contacted with gaseous epichlorohydrin for at least 30 seconds.

15 8. A process according to any of the preceding claims, in which the cellulosic material is heated to above the boiling point of epichlorohydrin after being contacted with the epichlorohydrin and before removal from the closed system.

20 9. A process according to any of the preceding claims, in which the cellulosic material is impregnated with moisture and strong base

by padding the material in an aqueous solution of the strong base to obtain a pick-up thereof of between 35% and 100%.

10. A process according to any of the preceding claims, in which the selected configuration of the cellulosic material is a smooth wrinkle-free configuration.

11. A process according to any of the preceding claims, in which the cellulosic material is cotton fabric.

12. A process according to claim 1 substantially as hereinbefore described with particular reference to the examples.

13. Cross-linked cellulosic material whenever prepared by the process of any of claims 1—12.

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